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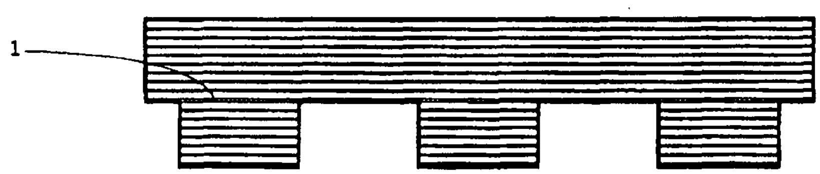
(54) Title: METHOD FOR FABRICATING METAL NANOSTRUCTURES



(57) Abstract

A method for fabricating nanostructures directly in a material film (3), preferably a metal film (3), deposited on a substrate (5) are disclosed. In a preferred embodiment a mold (1) or stamp (1) having a surface which is the topological opposite of the nanostructure to be created is pressed into a heated metal (3) coated on a substrate. The film (3) is cooled and the mold (1) is removed. In another embodiment, the thin layer of metal (3) remaining attached to the substrate (5) is removed using bombardment with a charged particle beam.

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Method for Fabricating Metal Nanostructures

Technical Field

The present invention is concerned with metal nanostructures, methods for fabricating them, and embodiments of the same.

Background Art

The development of low-cost, high-throughput techniques that can achieve resolutions of less than 50 nm is essential for the future manufacturing of semiconductor integrated circuits and the commercialization of electronic, opto-electronic, and magnetic nanodevices. Numerous technologies are under development. Scanning electron beam lithography has demonstrated 10 nm resolution; however, because it exposes point by point in a serial manner, the current throughput of the technique is too low to be economically practical for mass production of sub-50 nm structures. X-ray lithography has demonstrated 20 nm resolution in a contact printing mode and can have a high throughput, but its mask technology and exposure systems are currently rather complex and expensive. Lithographies based on scanning proximal probes, which have shown a resolution of about 10 nm, are in the early stages of development.

Conventional e-beam lithography involves exposing a thin layer of resist (usually a polymer film) coated on a metal film, itself deposited on a substrate, to an electron beam. To create the desired pattern in the resist, the electron beam is scanned across the surface in a predetermined fashion. The chemical properties of the resist are changed by the influence of the electron beam, such that exposed areas may be removed by a suitable solvent from the underlying metal film. The surface of the exposed metal film is etched, and finally unexposed resist is removed by the another solvent.

In the etching process, the isotropic properties of the metal mean that the etchant will etch in both depth and in a direction parallel to the substrate surface under the resist. The depth of etching under the resist is approximately the same as the thickness of the metallic film.

If this approach is used to create two metal strip lines which are as narrow as possible and separated by a minimum possible distance, then the under-etching means that the width of strip is decreased and the distance between the strips is increased. In addition, part of the resist under-etched can collapse, which makes the edge of the strip irregular, or break during subsequent fabrication steps.

Overall, this means that the width of the strip is less than desired, and the distance between the strips is more than planned. Very thin strips can be produced, but the minimum distance between strips is greater than wanted. In another words, strips can be made which are even less wide than the e-beam focusing dimension, but distance between strips is greater than expected. In addition non-regularities on the strip edges are obtained.

One approach to overcome the under-etch problem could be the use of focussed ion beam (FIB) processing. This approach is described in U.S. Patent No. 4,639,301 to Doherty et al., and uses an apparatus which makes possible the precise sputter etching and imaging of insulating and other targets, using a finely focused beam of ions. This apparatus produces and controls a submicron beam of ions to precisely sputter etch the target. A beam of electrons directed on the target neutralizes the charge created by the incident ion beam. The FIB system can precisely deposit either insulating or conducting materials onto an integrated circuit. However, this approach requires each item to be produced separately, and consequently is slow and expensive.

Another approach to creating nano-structures is described in a report in Science, Volume 272, April 5 1996, pages 85 to 87, entitled "Imprint Lithography with 25-nanometer Resolution", where Chou et al. demonstrate an alternative lithographic method, imprint lithography, that is based on compression molding and a pattern transfer process. Compression molding is a low-cost, high-throughput manufacturing technology that has been in use for decades and features with sizes of >1 μm are routinely imprinted in plastics. Compact disks based on imprinting in poly-carbonate are one example. Other examples are imprinted polymethylmethacrylate (PMMA) structures with a feature size on the order of 10 μm and imprinted poly-ester patterns with feature dimensions of several tens of micrometers. However, compression molding had not been developed into a lithographic method to pattern semiconductors, metals, and other materials used in semiconductor integrated circuit manufacturing.

Chou's approach uses silicon dioxide molds on a silicon substrate. The mold was patterned with dots and lines having a minimum lateral feature size of 25 nm by means of electron beam lithography, and the patterns were etched into the SiO_2 layer by fluorine-based RIE. This mold is pressed into a thin PMAA resist cast on a substrate, which creates a thickness contrast pattern in the resist. After the mold is removed, an anisotropic etching process is used to transfer the pattern into the entire resist thickness by removing the remaining resist in the compressed areas. This imprinted PMAA structure has structures with 25 nm feature size and a high aspect ratio, smooth surfaces

with a roughness of less than 3 nm and corners with nearly 90° angles. The structures, though of little use in nano-electronic devices, are useful as masters in a lift off process for making nano-structures in metals: 5 nm of Ti and 15 nm of Au are deposited onto the entire sample, and then the metal on the PMMA surface is removed as the PMMA is dissolved in acetone.

Chou's approach thus requires two stages to produce the finished metal structure: first, nanoimprint lithography into a polymer mold; and second a metal lift-off and reactive ion etch. The number of steps used will clearly bear on the difference between the original mold and the final product. In addition, the lift-off process destroys the polymer mold, which means that a new PMAA mold must be produced in each process cycle.

Disclosure of Invention

Broadly the present invention is a method for fabricating nano-structures directly in a film, preferably metal, deposited on a substrate. In a preferred embodiment a mold or stamp having a surface which is the topological opposite of the nano-structure to be created is pressed into a heated metal coated on a substrate. The film is cooled and the mold is removed.

In another embodiment, the thin layer of metal remaining attached to the substrate is removed using bombardment with a charged particle beam.

The mold can be fabricated using any known nano-fabrication techniques which allow anisotropic etching to achieve 90° angles. For example it can be made from an anisotropic material, such as single crystal silicon, so that etching, for example anisotropic reactive ion etching, can take place only in the direction normal to surface. The mold is made from a material which does not adhere to the metal used in order to avoid damage to the metal film structure in the process of removing mold. The mold material has a melting point higher than the metal film to avoid changes in mold shape during frequent imprinting.

An object of the present invention is to provide a method for creating nano-structures on the surface of a substrate by stamping a nano-structured mold or stamp into a softened film of material, preferably metal, coated on a substrate.

An advantage of the present invention is that the complex and costly process of e-beam lithography is used only once for making the mold or stamp, which can be used subsequently for the production of many hundreds of substrates having metal nano-structures on their surface.

Another advantage of the present invention is that the metal nano-structure is produced from the nano-structured mold or stamp in a single step.

A further advantage of the present invention is that the dimensions of the structures created is limited only by the focusing possibilities of the electron beam or ion beam used to fabricate the mold.

An object of the present invention is to provide a method for removing excess metal remaining on the substrate surface after the mold is removed which leaves 90^{o} angles in the nano-structure unchanged.

An advantage of the present invention is that removal of the thin layer of metal by means of bombardment with charged particles is easy to control and it simultaneously cleans the surface.

Brief Description of the Drawings

Fig. 1(a) - (d) is a schematic representation of a process for making a nano-structured surface in a metal film coated on a substrate.

Reference Numerals Used in the Drawings

1. Mold
3. Metal film
5. Substrate
7. Thin film of metal
9. Ion beam

Best Mode for Carrying Out the Invention

Referring now to Fig. **1(a)**, a mold **1** whose surface carries a nano-structure which is the topological opposite of the nano-structure pattern to be fabricated, in that the mold has protruding areas where indentations are desired in the final product, and carries indentations where protrusions are required in the final product, is pressed into a softened metal film **3** coated on a substrate **5**.

In preferred embodiments, the metal film is softened by heating. The pressure used for imprinting and film temperature should be adjusted for particular metal used.

The substrate is preferably silicon, but may be any material which has a melting or softening temperature greater than that of the metal-coating.

The metal used is preferably gold, but any metal which has a melting or softening temperature below that of the substrate material may be used.

Film **3** is cooled and mold **1** is removed to give the nano-structured surface shown in Fig. **1(b)**.

Mold **1** can be fabricated utilizing any of the known nano-fabrication techniques which permit anisotropic etching to achieve 90° angles. In a preferred embodiment it is made from an anisotropic material, most preferably single crystal silicon, so that etching, most preferably anisotropic reactive ion etching, can take place only in the direction normal to the surface. The mold is preferably made from a material which does not adhere to the particular metal used in order to avoid damage to the metal film structure when the mold is removed. In addition the mold material should have a melting point higher than that of the metal film to avoid changes in mold shape during frequent imprinting.

If the nano-structured surface is to comprise raised areas of metal on a substrate surface, the thin layer of metal **7** between the raised areas are removed using a charged particle beam **9**, as shown in Fig. **1(c)**. The charged particle beam may be electron beam, ion beam, or a magnetron method using high frequency fields._Beam intensity and exposure time are adjusted according to metal film thickness and imprinting depth.

This yields the nano-structured surface shown in Fig. **1(d)**.

Industrial Application

Thus the method for fabricating metal nano-structures on substrate surfaces described above is a low-cost, high-throughput technique that can achieve resolutions of less than 50 nm. The method will find wide applicability to manufacturing of semiconductor integrated circuits and the commercialization of electronic, opto-electronic, and magnetic nanodevices. In addition, these approaches for fabricating nano-structured surfaces will be of great utility in the construction of surfaces having enhanced electron emission such as those disclosed by Tavkhelidze et al in U.S. Pat. Appl. No. 09/045,299, entitled "Method for Manufacturing Low Work Function Surfaces", incorporated herein by reference in its entirety.

The invention should not be construed as limited to the specific embodiments and methods described above but should be seen to include equivalent embodiments and methods. For example, the substrate may be any material which has a melting or softening temperature greater than that of the metal-coating, and materials include silica, quartz, glass, diamond, and metal.

Furthermore, the material used to coat the substrate is specified as being a metal, but it may be any substance which has a melting or softening temperature below that of the substrate material, including metals such as silver, nickel, and titanium, alloys, semiconductor materials, superconductor materials or polymers.

Current lithographic techniques have been used to fabricate the mold, but other direct techniques are possible such as focused ion beam processing.

Claims

1. A method for fabricating one or several nano-structures on a surface of a substrate comprising the steps:

   (a) providing a substrate coated with a material,

   (b) forming said structures in said material coating by pressing into said material with a nano-structured mold.

2. The method of claim 1 in which said substrate is selected from the group consisting of: silica, quartz, glass, diamond, and metal.

3. The method of claim **1** in which said material is selected from the group consisting of metals, alloys, superconductors, semiconductors and polymers.

4. The method of claim **3** in which said metal is selected from the group consisting of gold, silver, nickel and titanium.

5. The method of claim **1** wherein said forming step comprises the steps of:

   (a) softening said material,

   (b) pressing into said material with a nano-structured mold to imprint said structure in said material coating,

   (d) hardening said material,

   (e) separating said material from said mold.

6. The method of claim **4** wherein said softening step comprises heating the material.

7. The method of claim **4** wherein said hardening step comprises cooling the material.

8. The method of claim **5** in which said material is selected from the group consisting of metals, alloys, superconductors, semiconductors and polymers.

9. The method of claim **8** in which said metal is selected from the group consisting of gold, silver, nickel and titanium.

10. The method of claim **1** additionally comprising the step of exposing said nano-structures to an ion beam to remove part of said material and

expose said substrate beneath indentations formed in said material film by said mold.

11. A mold for forming one or several nano-structures in the material of a material-coated substrate when pressed into said material-coated substrate.

12. A method for making the mold of claim **11** comprising the step of forming by lithography on the surface of a material structures whose topography is the opposite of said nano-structures to be formed.

13. The method of claim **12** in which said lithography step is selected from the group consisting of: electron beam lithography, X-ray lithography, scanning proximal probe lithography and focused ion beam lithography.

14. The method of claim **12** in which said material is single crystal silicon.

15. A method for fabricating one or several nano-structures on a surface of a substrate comprising the steps:

(a) providing a material-coated substrate,

(b) softening said material,

(c) pressing into said material with a nano-structured mold to imprint said structure in said material coating,

(e) hardening said material,

(f) separating said material from said mold,

(d) exposing said material nano-structures to an ion beam to remove part of said material and expose said substrate beneath indentations formed in said material film by said mold.

16. The method of claim **15** in which said substrate is selected from the group consisting of: silica, quartz, glass, diamond, and metal.

17. The method of claim **15** in which said material is selected from the group consisting of metals, alloys, superconductors, semiconductors and polymers.

18. The method of claim **17** in which said metal is selected from the group consisting of gold, silver, nickel and titanium.

19. The method of claim **15** wherein said softening step comprises heating the material.

20. The method of claim **15** wherein said hardening step comprises cooling the material.

Fig. 1(a)

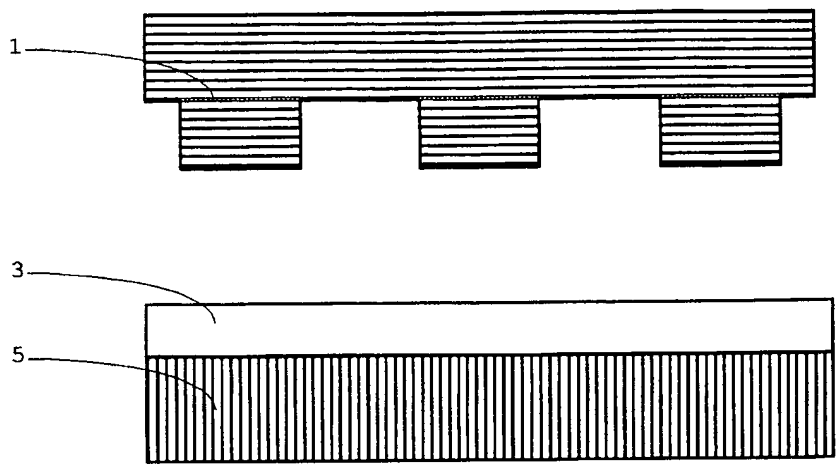


Fig. 1(b)

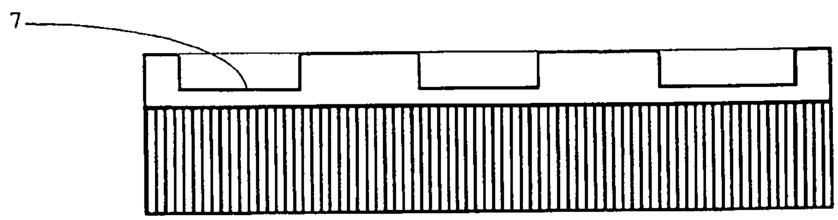


Fig. 1(c)

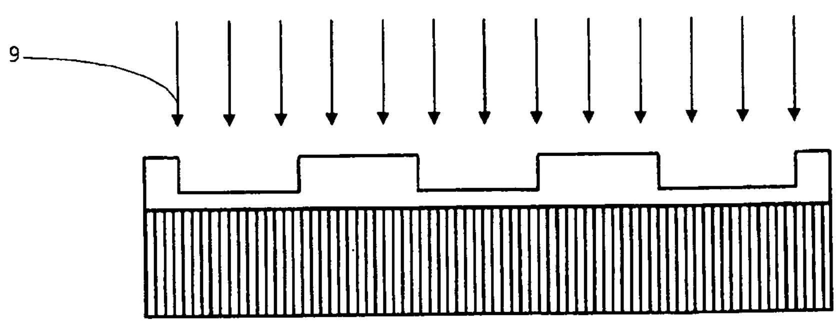
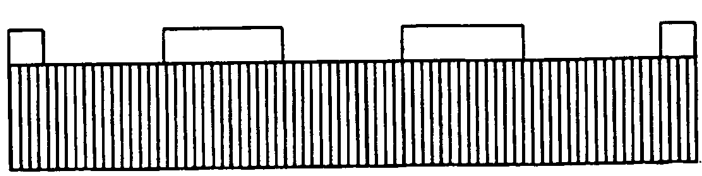


Fig. 1(d)



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C23C 14/34; B21B 45/00; B32B 3/26; G03C 5/00
US CL :Please See Extra Sheet.
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B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 29/825, 829, 846, 853; 204/192.34; 72/46, 47; 430/18, 296, 320, 966, 942; 264/107, 134, 139, 430, 447

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS
search terms: mold, press, emboss, ion beam, metal, layer, film, coating, stamp

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	CHOU et al, Imprint Lithography with 25-Nanometer Resolution, Science, Vol. 272, 05 April 1996, pp. 85-87.	1-8, 11-13 ----------- 4, 9, 14-20
Y	US 5,193,014 A (TAKENOUCHI et al) 09 March 1993, Column 5 lines 16-23, lines 62-68; Column 6 lines 1-7.	1-10, 15-20
A	US 4,639,301 A (DOHERTY et al) 27 January 1987, See Abstract; Fig. 1.	1-20
Y	US 4,407,695 A (DECKMAN et al) 04 October 1983, See Abstract; Column 6 lines 36-68.	10, 15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER:
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29/825, 829, 846, 853; 204/192.34; 72/46, 47; 430/18, 296, 320, 966, 942; 264/107, 134, 139, 430, 447